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The Solvent Extraction of Zinc Pivaloyltrifluoroacetate Adducts with Monodentate and Bidentate Ligands

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The effect of the monodentate and bidentate neutral ligands acting as a synergist on the extraction of zinc with pivaloyltrifluoroacetone was investigated. TPPO, TOPO and TPAsO were used as neutral monoxide ligands, MBDPO and EBDPO as dioxide ligands, pyridine, picolines and 2,6-lutidine as monodentate N-bases, and α,α' -dipyridyl and bathophenanthroline as bidentate N-bases. Ligands containing oxygen react with zinc chelate to form the adducts of $MR_2\cdot L$ type, and the stability constant of the adducts increases in the following order: TPPO < EBDPO < MBDPO < TOPO < TPAsO. The stability of adducts with pyridine bases increases in the order, 2,6-lutidine < α -picoline < pyridine < γ -picoline. A striking synergistic effect was observed in the presence of α,α' -dipyridyl and bathophenanthroline.

INTRODUCTION

The gas chromatograms of the metal chelates of such fluorinated β -diketones as 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione¹⁾ and pivaloyltrifluoroacetone²⁾ were successfully obtained. Recently, the gas chromatography of β -diketone adducts with some organophosphorus compounds has been reported.^{3,4)} The method is expected to have the advantages that non-volatile or unstable chelates are changed into volatile or more stable chelates by adduct formation and that the synergistic extraction caused by adduct formation produce high extractability of an aiming metal. Zinc β -diketonates are very difficult to be eluted, but the gas chromatograms of β -diketonate adducts with organophosphorus compounds were successfully obtained.⁵⁾

This synergistic enhancement of metal chelate extraction, which was at first reported by Cuninghame *et al.*,⁶⁾ has been found in various systems and reported by many investigators.⁷⁾ In our previous papers, the synergistic research was carried out on various metal β -diketone adducts.⁸⁻¹¹⁾ In one of the papers, the effect of terminal groups of the ligands and the relationship between central ion and the stability of the adducts were investigated.

The present work deals with the synergistic effect in the solvent extraction of zinc PTA chelate adducts with mono- and bidentate neutral ligands firstly in order to have the preliminary knowledge for their gas chromatographic measurement and secondly to compare the adduct stability of bidentate neutral ligands with that of monodentate ligands.

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EXPERIMENTAL

Apparatus and Reagents. Radioactivity countings were made with a TEN NaI (TI) (44.5 mm in dia. \times 50.8 mm) well-type scintillation counter, Model EA-14, connected with a Metro dekatron scaler, Model MCL-6B. A Hitachi-Horiba glass electrode pH meter, Model M-5, was used for the pH measurements.

The radioisotope, zinc-65 was supplied by the Oak Ridge National Laboratory, Oak Ridge, Tennessee, U. S. A., as chloride in hydrochloric acid solution. This was converted into the perchlorate and diluted with perchloric acid (0.01 M) to make the solution of about 1 μ Ci/ml. Sodium perchlorate was prepared by dissolving sodium carbonate in perchloric acid and purified by recrystallization from pure water.

Pivaloyltrifluoroacetone (PTA) was synthesized from pinacolin and trifluoroacetic acid.²⁾ Methylenebis(diphenylphosphine oxide), MBDPO, was synthesized by the hydrogen peroxide oxidation of methylenebis(diphenylphosphine) which was prepared from dichloroethane and sodium diphenylphosphide.¹²⁾ Ethylenebis(diphenylphosphine oxide), EBDPO, was also prepared by the same method. Triphenylarsine oxide, TPAsO, and triphenylphosphine oxide, TPPO, were prepared by oxidizing triphenylarsine and triphenylphosphine with hydrogen peroxide. Other organic bases—tri-*n*-octylphosphine oxide (TOPO), pyridine, α -picoline, γ -picoline, 2,6-lutidine, α, α' -dipyridyl and batho-phenanthroline—were obtained commercially. All the other reagents were GR grade materials and were used without further purification.

Procedure. The procedure of the solvent extraction was essentially the same as that described in previous papers.⁸⁾ Ten milliliters of an aqueous solution containing radioactive zinc, sodium perchlorate (0.10 M) and acetic acid (0.01 M) in a 30 ml glass-stoppered centrifuge tube were adjusted to a desired pH and were shaken with 10 ml of benzene containing 0.05 M of PTA and various concentrations of neutral ligand for one hour at about 25°C. After centrifugal separation, 2 ml of each phase were pipetted out into test tubes, and the γ -activities were measured with a NaI(Tl) scintillation counter. The pH value of the aqueous phase was checked after the extraction process.

Theoretical treatments are the same as the previous works.⁸⁾ The extraction constants of zinc chelate, K , and the stability constants of adducts, β_n , can be calculated by the following equations:

$$K = [ZnR_2]_0 [H^+]^2 / [Zn^{2+}] [HR]_0^2 \quad (1)$$

$$\log K = \log D - 2 \log [HR]_0 - 2 \text{ pH} \quad (2)$$

$$\beta_n = [ZnR_2L_n]_0 / [ZnR_2]_0 [L]_0^n \quad (3)$$

$$\log D^*/D = \log (1 + \sum_{n=1}^n \beta_n [L]_0^n) \quad (4)$$

where D and D^* are the distribution ratios in the absence and in the presence of a neutral ligand, HR and L stand for pivaloyltrifluoroacetone and neutral ligand, and $[\quad]$ and $[\quad]_0$ denote the concentration of the chemical species in the aqueous and organic phases, respectively.

RESULTS AND DISCUSSION

Curve I in Fig. 1 shows the D vs. pH plots on the extraction of zinc with PTA in absence of any adduct-forming ligands. The curve has an almost straight line with a slope of theoretical value, 2, when the concentration of PTA is kept constant. The logarithms of the distribution ratio of zinc are plotted in Fig. 1 (Curve II-VI) as a function of pH, when zinc is extracted with PTA in the presence of 10^{-3} M benzene solution of such neutral ligands as TOPO, TPPO, TPAsO, MBDPO and EBDPO. As shown in the figure, the extraction of zinc is enhanced in the following order; TPPO < EBDPO < MBDPO < TOPO < TPAsO.

In order to make the phenomenon clearer, the stability constants of the chelate adduct are analysed by Eq. 4. Figure 2 represents the change in the distribution ratio of zinc as a function of the concentration of neutral ligands. As the slope of asymptotes of curved plots or the linear slope of $\log D^*/D$ vs. $\log [L]_0$ indicates the maximum number of the

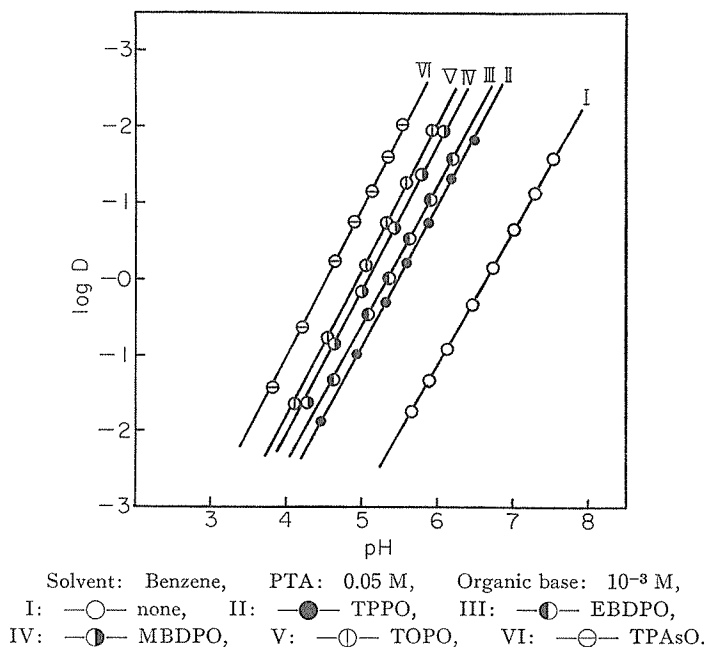


Fig. 1. Effect of pH in the synergistic extraction of zinc chelate with phosphine oxide base.

Table 1 Stability Constants of Zinc PTA Adducts with neutral Ligands.

neutral ligand	$\log \beta$	neutral ligand	$\log \beta$
TPPO	4.95	pyridine	5.15
TPAsO	6.67	α -picoline	4.90
TOPO	6.19	γ -picoline	5.31
MBDPO	5.72	2,6-lutidine	4.31
EBDPO	5.30		

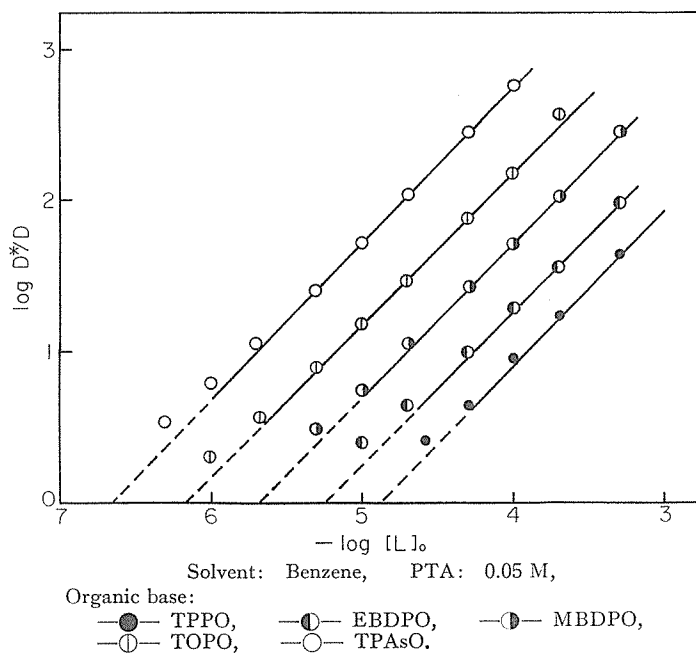


Fig. 2. Effect of phosphine oxide concentration in the synergistic extraction of zinc chelate system.

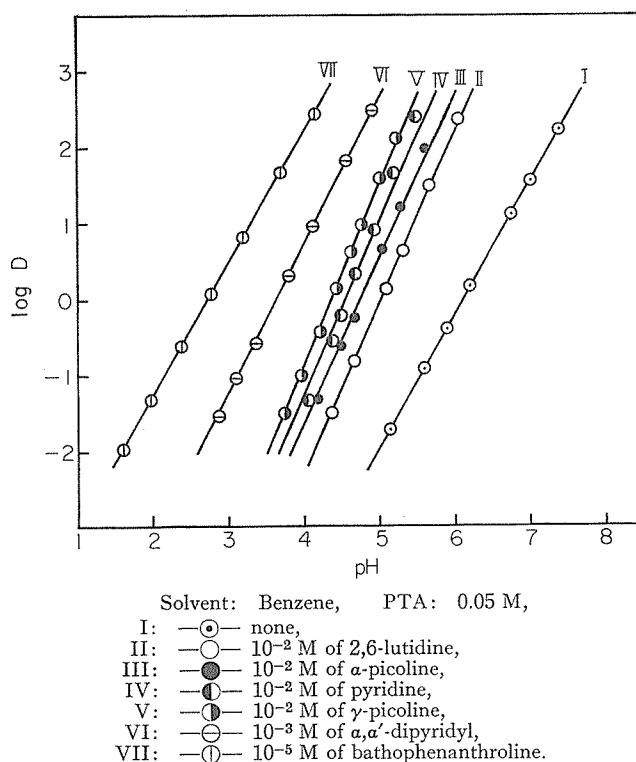


Fig. 3. Effect of pH in the synergistic extraction of zinc PTA chelate with pyridine base.

neutral ligand, zinc PTA chelate is considered to form $MR_2 \cdot L$ type adducts with both monoxides (TOPO, TPPO and TPAsO) and dioxides (MBDPO and EBDPO). The stability constants of the adducts, $\log \beta_1$, can be obtained from the plots in Fig. 2, and the results are summarized in Table I. It is observed that diphosphine dioxides may bond to the zinc PTA chelate as a monodentate ligand as well as to the zinc BFA chelate, though the dioxides behave as a bidentate ligand in the trivalent europium BFA chelate.¹¹⁾

The adduct stability constant of the zinc PTA chelate increases in the following order: TPPO < TOPO < TPAsO. This is the same as the order found with europium BFA chelate. The order of TPPO and TOPO may be mainly caused by the resonance effect or the interaction of π -electron of aromatic group with that of the phosphine oxide double bond. The higher stability of TPAsO than that of TPPO can be attributed to the increasement of dipole moment by the replacement of phosphine atom with arsine. The stability constant of TPAsO enhanced by the effect excels that of TOPO adduct.

The stability constants of zinc PTA chelate with MBDPO and EBDPO exist between TOPO's constant and TPPO's. As the aromatic groups are introduced from TOPO to TPPO, the basicity of the neutral ligands has a tendency to weaken in order. Therefore, when the phosphine oxides behave as monodentate ligands for the zinc PTA chelate, their stability constants are expected to become higher than that of TPPO. The MBDPO adduct of the zinc chelate is somewhat more stable than the EBDPO adduct. This may be caused by the stronger interaction between phosphine oxide groups.

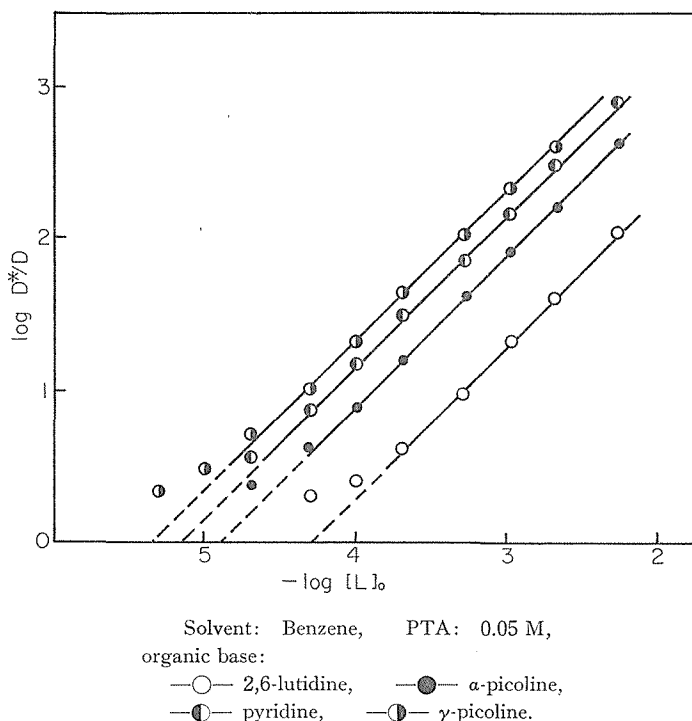


Fig. 4. Effect of pyridine base concentration in the synergistic extraction of zinc chelate system.

The stability constants of zinc PTA adducts with the mono- and bidentate ligands of *N*-containing heterocyclic bases were examined to compare the two neutral ligands. The $\log D$ vs. pH plots on the extraction of the zinc PTA chelate are shown in Fig. 3 when 10^{-2} M of γ -picoline, α -picoline, 2,6-lutidine, 10^{-3} M of α , α' -dipyridyl and 10^{-5} M of bathophenanthroline are present, respectively. The extraction of zinc is extremely enhanced by the addition of a small quantity of the bidentate heterocyclic ligands, as seen from the curves VI and VII in Fig. 3.

The plots of $\log D^*/D$ vs. $\log [L]_0$ on the extraction in the presence of such monodentate heterocyclic bases as pyridine and picolines are shown in Fig. 4, from which the stability constant of the adducts can be obtained. The asymptotes of the plots at infinite $[L]_0$ value in the figure give a slope of 1. This indicates the formation of the adduct with one mole of the monodentate heterocyclic ligand, such as $\text{ZnR}_2 \cdot \text{L}$. Stability constants obtained from the asymptotes, as summarized in Table I, rise in the following order: 2,6-lutidine < α -picoline < pyridine < γ -picoline. This order correlates not only with the basicity of the pyridine bases, but also with the steric effect of the methyl group in α -position: The higher stability of γ -picoline adduct than that of pyridine adduct reflects the increased basicity by introducing the methyl group, and the lower stabilities of α -picoline and 2,6-lutidine adducts are caused by the larger steric hindrance.

A striking synergistic effect is observed on the extraction of zinc chelate in the presence

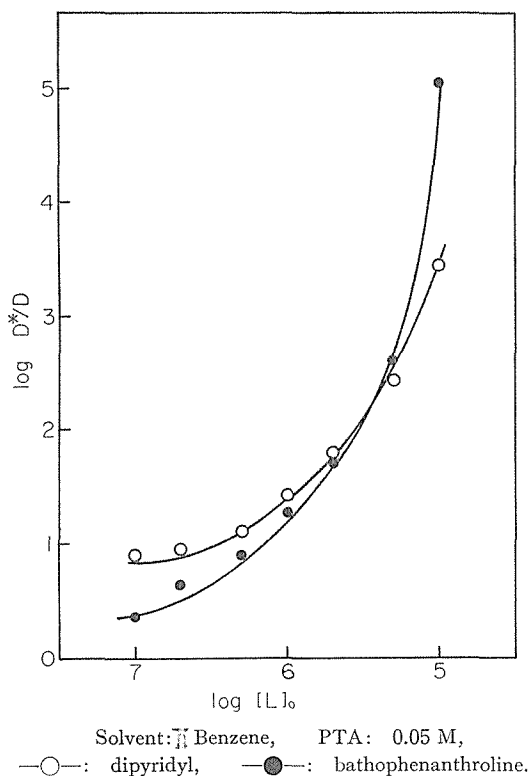


Fig. 5. Effect of bidentate pyridine base.

of a small amount of α,α -dipyridyl and bathophenanthroline. The change in the distribution ratio of zinc resulting from the addition of these ligands is shown in Fig. 5 as the $\log D^*/D$ vs. $\log [L]_0$ plots. It is supposed that the present ligands bond to the zinc chelate as a bidentate, judging from the strong synergistic extraction behavior. However, since the slope of asymptotes of the curved plots in Fig. 5 shows a strange change, clear analysis on the adduct formation is impossible. Further investigations will be necessary to dissolve this problem.

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